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DEVELOPMENT OF MANUFACTURING METHODS FOR HARD SUPERCONDUCTORS (WIRES AND RIBBONS)

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Electronics Branch
Manufacturing Technology Laboratory
Aeronautical Systems Division
Air Force Systems Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

ASD Project Nr. 7-993

A fabrication procedure has been developed and utilized to produce copper clad Nb_3Sn wires in lengths greater than 1000 ft. and niobium clad Nb_3Sn wires in lengths greater than 200 ft. Shorter lengths of ribbon of both materials have also been produced.

Prepared under Contract AF 33(657)-8800 by the Materials Research Corporation, Orangeburg, New York, G.T. Murray, et al.

NOTICES

FOREWORD

This Interim Technical Documentary Progress Report covers the work performed under Contract AF 33(657)-8800 from 20 June 1962 to 19 October 1962. It is published for technical information only and does not necessarily represent the recommendations, conclusions or approval of the Air Force.

This contract with the Materials Research Corporation, Orangeburg, New York was initiated under Project 7-993, "Pilot Plant Production of Hard Superconducting Wires and Ribbons". It is being accomplished under the technical direction of Mr. Harold K. Trinkle of the Electronics Branch, ASRCTE, Manufacturing Technology Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

Dr. G.T. Murray, the Corporation's Research Director was the engineer in charge. He was assisted by Mr. S. Hurwitt, Assistant Project Director. This report was given the Corporation internal number MRC 344.

This project is being carried out as a part of the Air Force Manufacturing Methods Program. The primary objective of the Air Force Manufacturing Methods Program is to develop on a timely basis manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. This program encompasses the following technical area:

> Rolled Sheet, Forgings, Extrusions, Castings, Fiber & Powder Metallurgy Component Fabrication, Joining, Forming, Materials Removal Fuels, Lubricants, Ceramics, Graphites, Non-metallic Structural Materials, Solid State Devices, Passive Devices, Thermionic Devices

Your comments are solicited on the potential utilization of the information contained herein as applied to your present or future production programs. Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

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PUBLICATION REVIEW

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ABSTRACT-SUMMARY
Interim Technical Documentary Report

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DEVELOPMENT OF MANUFACTURING METHODS
FOR HARD SUPERCONDUCTORS (WIRES AND RIBBONS)

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Materials Research Corporation

A fabrication procedure has been developed and utilized to produce copper clad Nb_3Sn wires in lengths greater than 1000 ft. and niobium clad Nb_3Sn wires in lengths greater than 200 ft. Shorter lengths of ribbon of both materials have also been produced.

The optimized fabrication procedure for these materials consists of a combination of rolling and drawing operations, the exact schedule being dependent on the metal sheath employed and the ultimate size desired. For copper clad material the composite is rolled to approximately 0.100" diameter and then drawn to final size. The niobium clad composites are rolled to about 0.125" diameter, inserted into a copper tube, rolled further to about 0.100" diameter, and then drawn to final size. Bare niobium clad specimens have also been rolled to a final size of 0.030" diameter.

The best niobium clad wire has shown a current density of 6×10^5 amp/cm^2 in a 15 kilogauss field on a 4" length 0.012" O.D. wire. The best copper clad specimen has shown a current density of 1.5×10^5 amp/cm^2 in zero field on a 4" length 0.030" O.D. wire. A 0.010" O.D. copper clad wire carried 7.2×10^4 amps/cm^2 at zero field.

Pertinent process variables that have been established are as follows:

(a) 16 hr. at 1000°C is sufficient for preforming the Nb_3Sn powder.

(b) A minimum of 16 hr. at 950°C is required for the final anneal.

(c) Air or water quenches from the final anneal are satisfactory but furnace cooling impairs the superconducting properties.

(d) Swaging operations should not be used in the reduction process.

DEVELOPMENT OF MANUFACTURING METHODS FOR HARD SUPERCONDUCTORS (WIRES AND RIBBONS)

I. INTRODUCTION:

The overall objective of the work on contract AF 33(657)-8800 was to develop a process for the fabrication of reliable hard superconducting wire and ribbon of a minimum critical field of 100,000 gauss at 4.2°K, critical temperature greater than 17°K, and critical current greater than 10^5 amp/cm^2 in a high gauss magnetic field, at 4.2°K, and to demonstrate the feasibility of this process through pilot line fabrication of 3000 ft. lengths. The niobium-tin system was selected as most likely to meet all of these requirements and the work to date has concentrated on this material. The first phase of this work was to study the processing parameters and design a pilot line capable of producing this wire and ribbon at a minimum rate of 500 ft./hr.

II. REVIEW:

The superconducting compound Nb_3Sn, is probably the most investigated high transition temperature material at present. This compound was first shown to be superconducting and to possess a transition temperature of 18.1°K by Matthias and co-workers (1)*. Being an intermetallic compound, this material is quite brittle and until recently has only been evaluated on specimens of short length. Kunzler, et al. (2), of Bell Laboratories, using short specimens, measured current densities of 1.5×10^4 amp/cm^2 in a magnetic field as high as 88,000 gauss. It is later shown (3) that relatively long lengths of wire containing Nb_3Sn core could be fabricated as follows: mixtures of Nb and Sn fine powders were pressed into the form of cylindrical slugs and placed into a niobium tube of 0.528" diameter. The composite was then cold drawn to 0.250" diameter, inserted into a nickel tube, and further cold drawn to 0.032" diameter wire. The wire was then heat treated for 16 hrs. in vacuum at 1000°C to produce the Nb_3Sn compound. A slight excess of Sn appeared to enhance the superconducting properties. Although some breakage was encountered in drawing, this wire reportedly possessed sufficient ductility that it could be bent around a 1/4" diameter mandrel. Presumably this bending was done prior to the compound formation anneal and thus had no bearing on the superconducting properties.

*Numbers in parentheses indicate references.

V.D. Arp, et al. (4), of the National Bureau of Standards, fabricated wire similar to that at Bell Laboratories except that the wire was swaged to a final diameter of 0.5 mm. Specimens of 12 cm length were etched and tinned on the ends with indium to which potential leads were soldered. Current densities of the order of 10^5 amp/cm^2 were measured at 1.6°K and the critical fields were found to be of the order of 188,000 gauss. This higher field strength was attributed to the prevention of joule heating by utilization of good contacts and AC pulse measurement techniques. (The current was measured in a parallel field.)

Betterton, et al. (5), of Oak Ridge National Laboratories, prepared Nb_3Sn specimens in a manner identical to the Bell Laboratories procedure and measured critical current as a function of field at 4.2°K by the pulsed-field, pulsed-current technique. Specimens were 0.38 mm diameter by 2.5 cm in length. Current capacities of the order of 1.8 X 10^5 amp/cm^2 at zero field were measured. In a transverse field this capacity decreased to 1.5 X 10^3 amp/cm^2 at 90,000 gauss. A similar specimen yielded considerably lower values. One niobium-tin 28,000 gauss superconducting magnet has been reported in the literature (6). This magnet consisted of three separate windings of 0.020" O.D. wire (2800 ft. total length) yielding an outside diameter of 3 inches.

The inability to achieve long lengths of wire of the same current carrying capacity as the best measured laboratory short lengths has hampered the development of high field magnets. The retainment of good superconducting after bending the wire around diameters of the order of 1/2" is also a problem that apparently has not been completely solved.

III. EXPERIMENTAL PROCEDURES:

(1) Wire and Ribbon Fabrication

The MRC process differs from that of other investigators in that the Nb_3Sn compound is preformed by reacting elemental powders in the form of pressed pellets. These pellets are then crushed, seived, packed into a metal tube, the tube reduced to wire or ribbon form and finally annealed. Numerous variables in this process have been investigated these include:

(a) Pellet composition - 20 to 25 at.% Sn.

(b) Pellet reaction anneal time - 16 to 72 hr. at 1000°C.

(c) Type of metal tube - niobium, nickel, and copper.

(d) Method of reducing packed tube - swaging, drawing, and rolling.

(e) Sintering time and temperature at final wire or ribbon size - 2 to 66 hr. at temperatures varying from 600 to 1000°C.

(f) Cooling rate from the sintering anneal - water quench, air quench, and furnace cool.

(2) Measuring Techniques

(a) Transition Temperature

A probe containing two specimens and a carbon resistor thermometer sealed in silicone oil is placed in a 25 litre dewar of liquid helium. The temperature of the probe tip is varied by changing its position above the liquid-gas interface. Temperatures from 4.2° to about 30°K can be maintained to ± 0.1°K. A 4 point measurement determines the resistivity of the specimen as the temperature is slowly changed.

(b) Current Carrying Capacity

A 38,000 gauss magnet constructed at MRC from 0.010" Wah Chang niobium zirconium wire is shown in Figure 1. The working field volume is 1" diameter by 4" length, allowing adequate room for insertion of specimens perpendicular to the field direction. Niobium and copper sheathed specimens were measured in this magnet at 4.2°K with the field both parallel and transverse to the specimen axis. The liquid helium transfer tube, the dewar containing the magnet, and the measuring apparatus is shown in Figure 2.

Prior to the completion of this magnet numerous current capacity measurements were made at zero field on specimens clad in copper only. Since copper is non-superconducting at 4.2°K the current measured is that carried entirely by the core. Voltage leads were attached with indium solder and using a

Keithley mille-micro voltmeter, voltage readings of 10^{-7} volts could be easily detected. In most cases the specimen return to the normal state as a function of current increase was manifested by a sharp sudden off-scale movement of the voltmeter needle. The results quoted in the following section will be that for a maximum 10^{-6} volt reading on the scale, although the voltage reading was often much less.

IV. RESULTS:

(1) Transition Temperatures:

In the absence of a magnet facility early in the program, transition temperatures were measured on numerous niobium-clad specimens to screen the process variables. For a given wire a sufficiently large number of short sections were tested to give an indication of the reliability of the fabrication process. Although these measurements yielded no information on current carrying capacity, the presence of a few sections (e.g. 10%) showing either a broad transition or only the niobium sheath transition was accepted as evidence of an undesirable process variable.

Typical transition curves of wire and ribbon are shown in Figure 3. The pellets were heated in vacuum for 72 hr. at 1000°C and water quenched. Other experiments in which the pellets were heated for periods varying from 16 to 72 hr. yielded similar results. The excess niobium wire (specimen A - 80 at.% Nb) showed essentially the same transition behavior as did the stoichiometric Nb_3Sn compositions.

The wire for specimen (A) was fabricated by swaging the packed niobium tube from 0.250" to 0.125" diameter, inserting this tube into a nickel tube and swaging the composite to 0.090" diameter, and finally drawing to specimen sizes of 0.020" and 0.010" diameters. The wire for curve (B) was fabricated by a combination of rolling and drawing operations. The packed niobium tube was rolled from 0.250" to about 0.125", inserted

Note 1: Measurements in higher fields (at 4.2°K) were performed at NASA, Lewis Research Center and the M.I.T. Magnet Laboratory. Specimens varying in length from 4 to 18 inches were used for these measurements.

into a copper tube, rolled further to about 0.100" diameter and finally drawn to 0.018". The wire for curve (C) was fabricated similarly except that the copper tube was omitted. The 0.030" wire was flat rolled to 0.005" thick ribbon. The core cross-sections for the rolled and drawn material was much more uniform than for the wires in which a swaging operation was utilized at some point in the process. The uniform structures for typical wire and ribbon specimens are shown in Figures 4 and 5 respectively. The swaged material on the other hand showed a very irregular shaped core. As a result, about 10% of the 10 to 15 specimens cut from 100 ft. length wires showed either broad transitions or only the niobium sheath transition. The rolled and drawn material showed no inferior transition behavior out of the same number of specimens tested. Numerous other experiments also conclusively demonstrated that swaged material was inferior to the rolled and drawn material.

Other experiments were conducted to determine the optimum sintering temperature and cooling rate therefrom. These results, shown in Figure 6, can be explained on the basis of the phase diagram determined by Reed, et al. (7) which shows that the superconducting compound Nb_3Sn is stable only above $\sim$875°C. Below 800°C two other compounds appear of which only one is superconducting. Thus, slow cooling rates and low sintering temperatures cause less superconducting material to be present in the core.

Figure 7 demonstrates that the transition characteristics do not change after cold bending (room temperature) the material. This ribbon was measured before and after being bent about a 0.5" diameter mandrel.

(2) Current Density

Because of the magnetic field requirement for current density determinations, relatively few specimens have been measured with respect to this parameter to date. The pertinent results obtained on niobium clad material are listed in Table I. The ribbon specimens were prepared by grooved rolling the bare niobium clad composite to about 0.035" diameter and then flat rolling to final thickness. The remaining wires were groove rolled to about 0.125" diameter, inserted into a thin wall copper sheath, swaged to about 0.050" diameter and then drawn to final size.

A sufficient number of specimens were measured to indicate the effect of the variation of composition and pellet reaction time at 1000°C. Comparing specimens 4, 5 and 6, with specimens 8, 9 and 10, it is evident that the higher niobium content material yields slightly lower current densities than does the stoichiometric composition. Specimen numbers 3 and 11 show that pellet reaction periods in excess of 16 hr. tends to reduce the current carrying capacity. Specimen number 7 shows that bending about a 0.75" diameter mandrel after heat treatment only slightly reduces the current carrying capacity. (The transverse field and longer specimen employed on the bent specimen must be taken into consideration here.)

The 15 Kg. field measurements were made more recently than the 100 and 35 Kg. field measurements. It is evident that this more recent material is far superior to the earlier fabricated wire and ribbon (after making a liberal allowance for the difference in field). This improvement is attributable to the introduction of the rolling and drawing practice. Early fabrication procedures, employed on specimens 1, 2 and 3, included a swaging operation. The transition temperature data showed that a large number of specimens must be measured to obtain a true picture of the behavior of swaged material. The more recently fabricated wire will be tested in high fields within the near future.

Experiments were conducted in an effort to eliminate the niobium sheath. Preformed and crushed Nb_3Sn powder was packed directly into nickel and into copper tubes and these then reduced by a combination of rolling and drawing operations; the latter operation being introduced at about a 0.090" diameter. It was found by microscopic examination after the sintering anneal that the nickel sheath reacted with the powders and reduced the effective core area. However, no reaction with the copper tube could be observed. The absence of the superconducting niobium sheath permitted the measurement of current densities at zero field. This parameter, rather than the transition temperature was used for cursory evaluation of the process variables of interest. The results on wires of the same composition and treatment but of different diameters are listed in Table II. The current densities varied by a factor of two but showed no relationship to wire size.

Since the current densities on the copper clad specimens were somewhat smaller than expected, attempts were made to enhance the current carrying capacity by varying the sintering time and the cooling rate from the sintering temperature. These results, all on the specimens from the same wire, are shown in Table III. Although some increase in current capacity was achieved by increasing the sintering time, it appeared that a limit was being approached and that longer sintering periods would not be worthwhile. Air cooling the sintered wires yielded about the same results as obtained by water quenching. Furnace cooling, on the other hand, definitely caused deterioration of the superconducting properties.

A few copper clad specimens of about 16" length were measured in transverse fields up to 83 Kg. at the M.I.T. Magnet Laboratory. Specimens from wire 33 (16 hr. at 950°C and water quenched) showed the best results. The variation of the current with field is shown in Figure 8. These current values were those which yielded a voltage drop of 10^{-7} volts on about a 1 inch specimen gage length. The current capacity of this wire (core $\sim$ 0.010" diameter) is 7×10^4 amp/cm^2 at 15 kilogauss transverse field and thus is about a factor of 4 lower than for a similar transverse field on niobium clad specimens (see specimen number 7, Table I). The copper clad specimens, on the other hand, are more readily fabricable. Lengths in excess of one thousand feet have been produced with ease. A 1000 ft. solenoid wound from such wire is shown in Figure 9.

V. DISCUSSION:

The fabrication procedure developed and reported here for the production of hard superconducting wire and ribbons consists of a combination of rolling and drawing operations, the exact schedule depending on the metal sheath employed and the ultimate size desired. Copper sheathed composites fabricate without difficulty and are reduced to size easily by either rolling and/or drawing operations. Niobium strain-hardens more than does copper during drawing and is also prone to die seizure when being drawn to size. It is thus desirable to minimize the drawing operation when working with niobium sheathed composites.

The niobium drawing difficulties can be minimized by jacketing the niobium sheath with copper or nickel. This technique has been employed by others as well as in the current work. However, it has the disadvantage that current capacity is sacrificed based on final wire diameter. Experiments are currently in progress with the object to circumvent this problem by annodization of the bare niobium sheath prior to drawing.

To date the niobium clad specimens have consistently shown higher current densities than copper clad specimens. Although microscopic examination did not reveal any reaction between the core and copper sheath, it is conceivable that copper atoms diffused into the core sufficient to reduce its current carrying capacity.

VI. FUTURE WORK:

Since only the niobium clad wires appear satisfactory at the moment for the construction of a 100,000 gauss magnet, work during the next quarter will concentrate on two major areas: firstly, fabrication and testing of niobium clad wires in lengths greater than 1000 ft. with the ultimate being an operating 60 kilogauss magnet for final check of the entire procedure. A large high temperature vacuum furnace has been constructed (Figure 10) and is currently being tested for the heat treatment of large solenoids.

Secondly, the copper clad process, though appearing less promising than the niobium clad composite, will be pursued further in view of the extreme ease of fabrication. Experiments to enhance the current capacity will include investigations of core composition, powder particle size, and sintering treatment. Work will also continue along these same lines on the niobium sheath process in the belief that the current capacity of the core in both processes is dependent on the amount of Nb_3Sn present. Current densities will be measured on coils greater than 1000 ft. in length, designed to create their own magnetic field.

VI. REFERENCES:

1. Matthias, B.T., Geller, S., and Goldstein, M., J. Am. Chem. Soc., Vol. 77, p. 1502 (1955).

2. Kunzler, J.E., Buehler, E., and Hsu, F., Physical Review Letters. Vol. 6, p. 89 (1961).

3. Olsen, K.M., Fuchs, E.O., and Jack, R.F., J. of Metals, p. 724 (October, 1961).

4. Arp, V.D., et al., Physical Review Letters, Vol. 6, p. 452 (1961).

5. Betterton, J. et al., Physical Review Letters, Vol. 6, p. 532 (1961).

6. Salter, L.C. et al., Proceedings of International Conf. on High Magnetic Fields, p. 344, M.I.T. Press and John Wiley; (1961).

7. Reed, T.B., et al., Lincoln Laboratory Preprint MS-512, 1962.

TABLE I

CURRENT CAPACITY OF NIOBIUM SHEATHED SPECIMENS AT

4.2°K (10^{-6} VOLTS MAX.)

Spec. No.	Treatment*	Maximum** Field (K gauss)	Maximum Current Amp.	Current Density in Core Amp/cm^2
1	0.005" x 0.100" rolled ribbon, 75 at.% Nb, pellets heated 48 hr.	100	25	3.0×10^4
2	0.005" x 0.125" rolled ribbon, 75 at.% Nb	35	135	4.5×10^4
3	0.005" x 0.100" rolled ribbon, 75 at.% Nb, pellets heated 32 hr.	35	80	4.0×10^4
4.	0.012" O.D. wire, 75 at.% Nb	15	75	6.0×10^5
5	"	15	64	5.0×10^5
6	"	15	50	4.0×10^5
7	0.012" O.D. wire, 75 at.% Nb, cold bent about 0.75" dia. mandrel	15	37	3.0×10^5
8	0.014" O.D. wire, 80 at.% Nb	15	40	2.5×10^5
9	"	15	40	2.5×10^5
10	"	15	70	4.4×10^5
11	0.028" O.D. wire, 75 at.% Nb, pellets heated 48 hr.	15	165	1.0×10^5
12	"	15	165	1.0×10^5

*Except where noted, pellets were formed by 16 hr. anneal at 1000°C and the final wire or ribbon was heated for 16 hr. at 950°C.

**All fields were parallel to specimen, except for specimen No. 7 which was transverse.

TABLE II

CURRENT CARRYING CAPACITY OF COPPER CLAD WIRES AT 4.2°K AND ZERO FIELD

Spec. No.	Wire No.	Wire Size	Final Anneal	Current (amp.)	Current Density in Core (amp/cm^2)
1	28	0.027	16 hr. 950°C, H_2O quench	75	7.0×10^4
2	33	0.018	"	54	1.2×10^5
3	33	0.010	"	9	7.2×10^4
4	36	0.030	"	165	1.5×10^5

TABLE III

CURRENT CAPACITY AT 4.2°K AND ZERO FIELD OF
COPPER CLAD WIRES AFTER VARIOUS SINTERING TREATMENTS

Spec. No.	Wire No.	Wire Size	Final Anneal	Current (amp.)	Current Density in Core (amp/cm^2)
1	30	0.030	4 hr. 950°C, H_2O quench	20	1.8×10^4
2	30	0.030	16 " " "	30	2.7×10^4
3	30	0.020	66 " " "	22	4.4×10^4
4	30	0.020	16 " " air cooled	17	3.4×10^4
5	30	0.020	16 " " furnace cooled	11	2.0×10^4

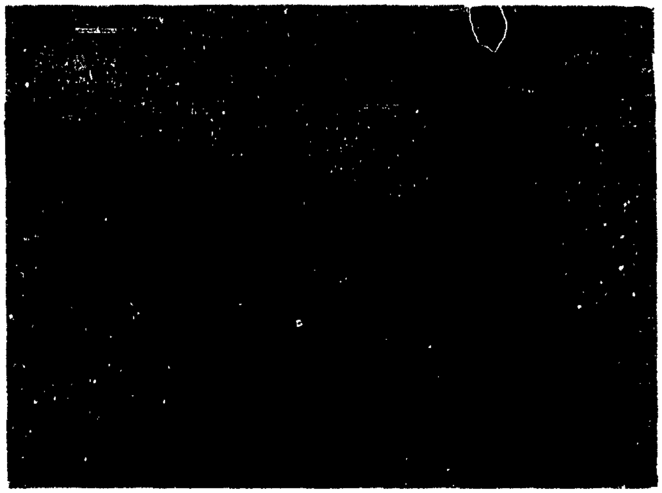

Figure 1. 38 kilogauss niobium-zirconium magnet

Figure 2. Liquid helium dewar containing magnet and specimen

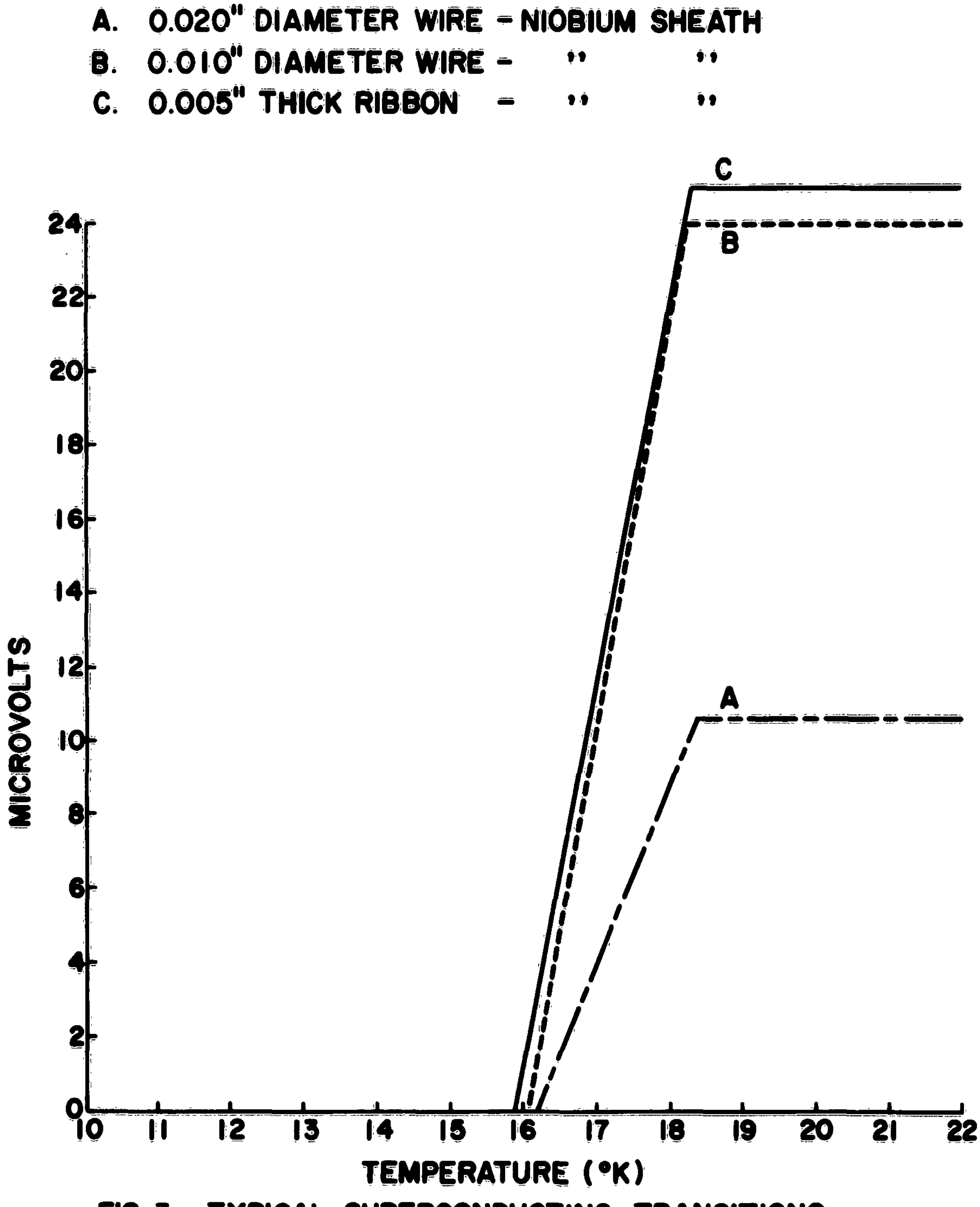

FIG. 3. TYPICAL SUPERCONDUCTING TRANSITIONS.

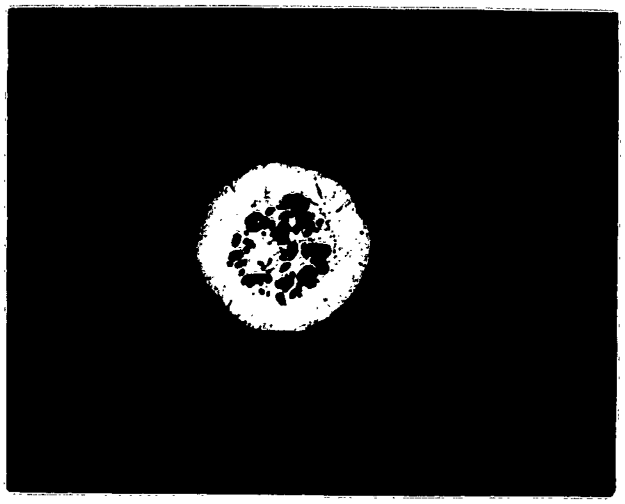

Figure 4. Cross-section of niobium clad wire; 0.013" O.D., Mag. 100X

Figure 5. Cross-section of niobium clad ribbon; 0.005" thickness, Mag. 25X

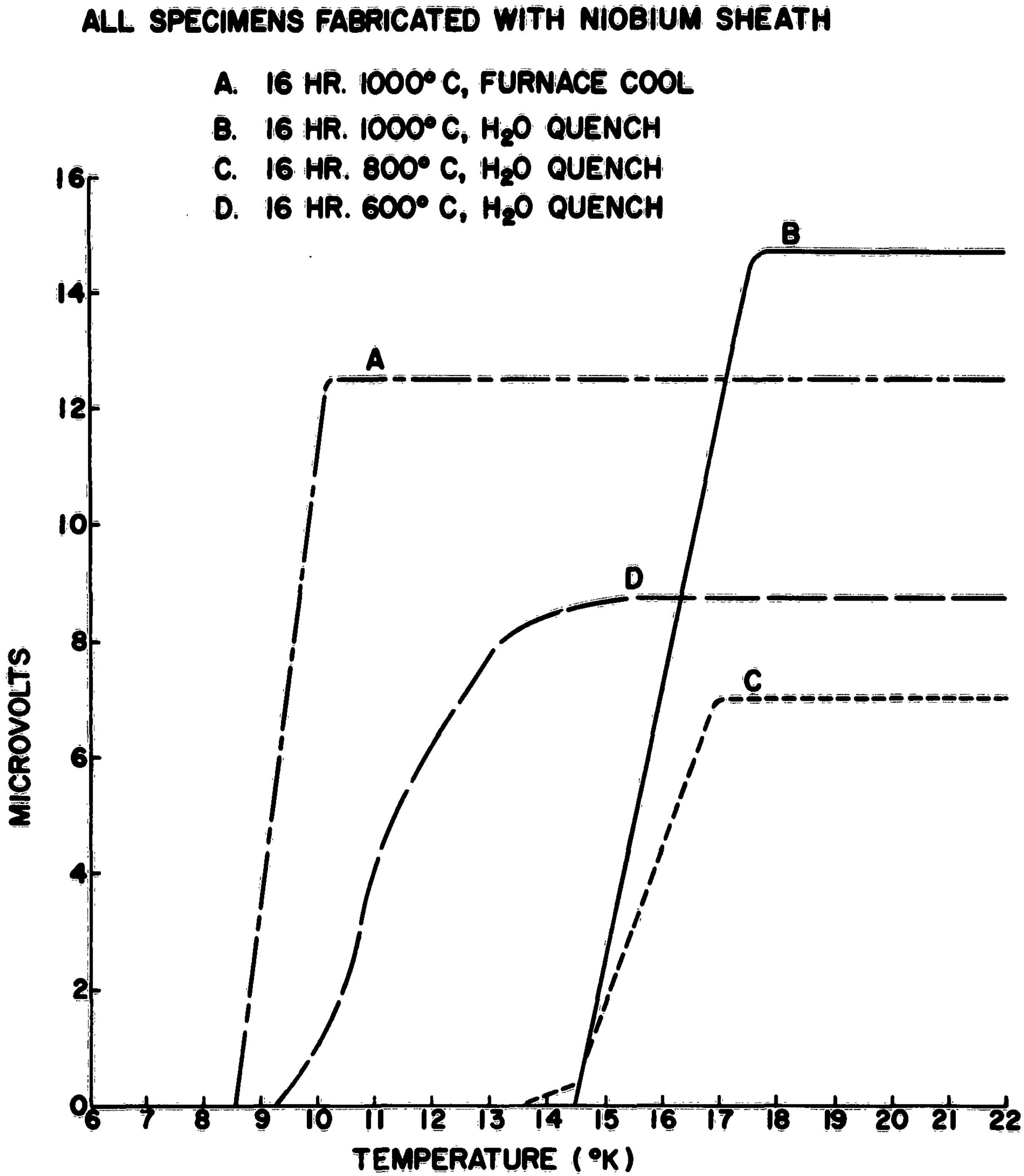

FIG. 6. EFFECT OF SINTERING TEMPERATURE AND COOLING RATE ON SUPERCONDUCTING TRANSITION.

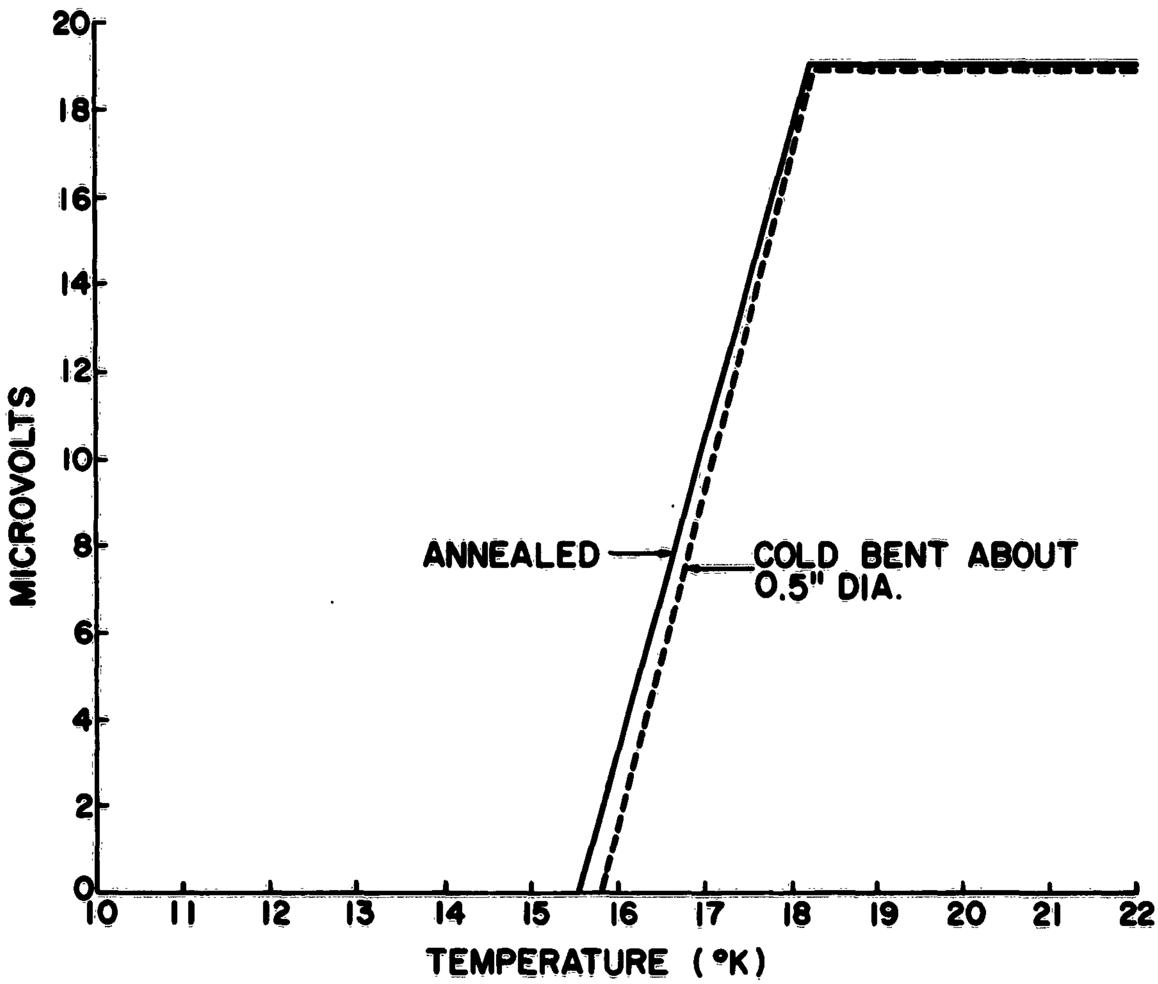

FIG. 7. EFFECT OF BENDING AT ROOM TEMPERATURE ON THE SUPERCONDUCTING TRANSITION OF NIOBIUM SHEATH RIBBON.

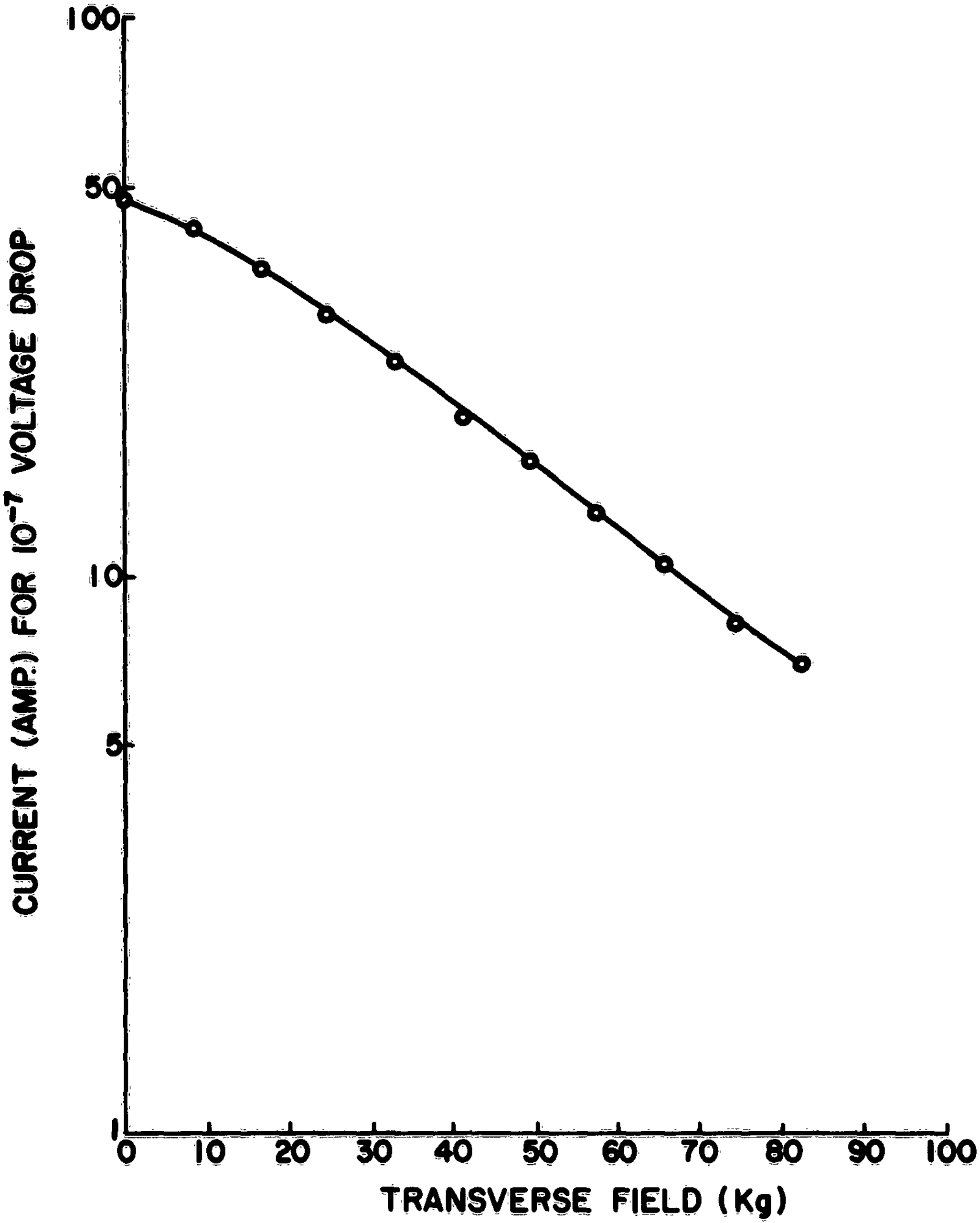

FIG. 8. CURRENT FOR 10^{-7} VOLTAGE DROP AS FUNCTION OF TRANSVERSE FIELD. COPPER CLAD 0.020" DIAMETER WIRE. COLD BENT ABOUT 3/4" DIAMETER.

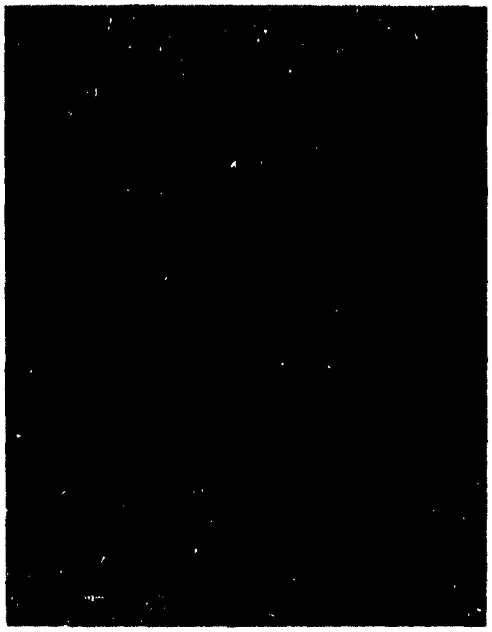

Figure 9. 1000 foot copper clad solenoid

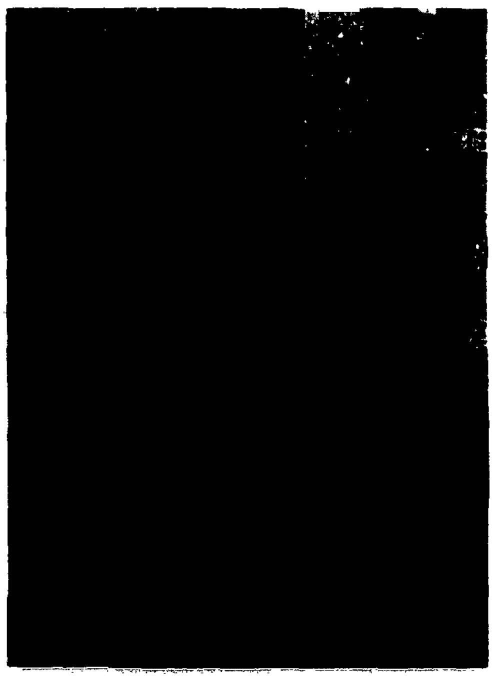

Figure 10. High temperature - high vacuum annealing furnace